AD-A284 873

(1)

OFFICE OF NAVAL RESEARCH

CONTRACT N00014-90-J-1212

R & T Code 4133008
Robert J. Nowak, Program Manager Electrochemistry

FINAL REPORT

ELECTROCHEMICAL INTERFACES AND ELECTRODE PROCESSES: ELECTROCHEMICAL OXIDATION OF SMALL ORGANISMS

by

Ernest B. Yeager

Case Western Reserve University
Case Center for Electrochemical Sciences and the
Department of Chemistry
Cleveland, Ohio 44106-7078

September 1, 1994

DTIC
ELECTE
SEP 2 8 1994
S
F

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale;
its distribution is unlimited.

DTIC QUALITY INSPECTED 3

24P 94-30936

404239

94 9 27 119

FINANCIAL STATUS REPORT

(Follow instructions on the back)

1. FEDERAL AGENCY AND ORGANIZATIONAL ELEMENT TO WHICH REPORT IS SUBMITTED	2. FEDERAL GRANT OR OTHER IDENTIFYING NUMBER	OMB Approved No. 80-R0180	PAGE	OF
Office of Naval Research	N00014-90-J-1212		1	1 PAGES

3. RECIPIENT ORGANIZATION (Name and complete address, including ZIP code)	4. EMPLOYER IDENTIFICATION NUMBER	5. RECIPIENT ACCOUNT NUMBER OR IDENTIFYING NUMBER	6. FINAL REPORT	7. BASIS
CASE WESTERN RESERVE UNIVERSITY UNIVERSITY WEST - 3RD FLOOR CONTROLLER'S GRANTS ACCOUNTING 10900 EUCLID AVE. 10. CLEVELAND, OH 44106-7006	13410108992A1	342-7453	[X] YES [ ] NO	[X] CASH [ ] ACCRUAL

8. PROJECT/GRANT PERIOD (See instructions)		9. PERIOD COVERED BY THIS REPORT	
FROM (Month, day, year)	TO (Month, day, year)	FROM (Month, day, year)	TO (Month, day, year)
10/1/89	9/30/93	10/1/89	9/30/93

PROGRAMS/FUNCTIONS/ACTIVITIES ►	(a)	STATUS OF FUNDS (b)	(c)	(d)	(e)	(f)	TOTAL (g)
a. Net outlays previously reported	$ 0.00	$	$	$	$	$	$
b. Total outlays this report period	350,000.00						
c. *Less:* Program income credits	0.00						
d. Net outlays this report period (*Line b minus line c*)	350,000.00						
e. Net outlays to date (*Line a plus line d*)	350,000.00						
f. *Less:* Non-Federal share of outlays	0.00						
g. Total Federal share of outlays (*Line e minus line f*)	350,000.00						
h. Total unliquidated obligations	0.00						
i. *Less:* Non-Federal share of unliquidated obligations shown on line h	0.00						
j. Federal share of unliquidated obligations	0.00						
k. Total Federal share of outlays and unliquidated obligations	350,000.00						
l. Total cumulative amount of Federal funds authorized	350,000.00						
m. Unobligated balance of Federal funds	0.00						

11. INDIRECT EXPENSE	a. TYPE OF RATE (Place "X" in appropriate box) [ ] PROVISIONAL [ ] PREDETERMINED [X] FINAL [ ] FIXED			
	b. RATE	c. BASE	d. TOTAL AMOUNT	e. FEDERAL SHARE
	50.51%	232,733.39	117,397.85	117,266.61

12. REMARKS: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.

13. CERTIFICATION

I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.

SIGNATURE OF AUTHORIZED CERTIFYING OFFICIAL: Anthony F. Braidic

DATE REPORT SUBMITTED: 12/13/93

TYPED OR PRINTED NAME AND TITLE: Anthony F. Braidic, Assistant Controller

TELEPHONE (Area code, number and extension): (216) 368-4280

269-102

STANDARD FORM 269 (7-76)
Prescribed by Office of Management and Budget
Cir. No. A-110

Accession For		
NTIS CRA&I	[X]	
DTIC TAB	[ ]	
Unannounced	[ ]	
Justification		
By		
Distribution /		
Availability Codes		
Dist	Avail and / or Special	
A-1		

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	Sept. 1, 1994	Final Report oct. 1, 1989 - Sept. 30,'93

4. TITLE AND SUBTITLE
Electrochemical Interfaces and Electrode Processes

5. FUNDING NUMBERS
Contract N00014-90-J-1212
Robert J. Nowak
R & T 4133008

6. AUTHOR(S)
Ernest B. Yeager

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Case Western Reserve University
Dept. of Chemistry
10900 Euclid Avenue
Cleveland, OH 44106-7078

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
Chemistry and Physics Division
Ballston Tower, Room 503
800 North Quincy St., Alexandria, VA 22217-5660

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Reproduction inwhole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; itsdistribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

This report summarizes research involving mechanistic studies of the oxidation of small hydrocarbons and carbon monoxide on platinum in aqueous electrolytes, transition metal oxides as electrocatalysts for O_2 reduction and as supports for dispersed platinum, and transition metal complexes exhibiting high catalytic activity for O_2 reduction on graphite. This research has been pursued principally by graduate students, using the research for the Ph.D. dissertation.

14. SUBJECT TERMS
Electrochemical oxidation of hydrocarbons and CO, transition metal oxides as electrocatalysts, transition metal complexes as electrocatalysts

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	NONE

FINAL REPORT

I. Summary of Research

A. Objectives of Contract Research

The overall objective of this ONR contract research has been to understand the factors controlling the activity of various electrocatalysts and to use this information as a guide to new catalysts and optimization of presently available catalysts. This research has involved the following areas:

- mechanistic studies of the oxidation of small hydrocarbons and carbon monoxide on platinum in aqueous electrolytes
- transition metal oxides as electrocatalysts for O_2 reduction and as supports for dispersed platinum
- transition metal complexes exhibiting high catalytic activity for O_2 reduction on graphite

This research has been pursued principally by graduate students, using the research for the Ph.D. dissertation.

B. Research Approach and Scientific Conclusions

1. Electrochemical oxidation of small organic molecules: ethane and ethylene

The oxidation of ethane and ethylene has been examined using linear potential sweep and potential step methods with single crystal platinum as well as polycrystalline platinum surfaces at temperatures up to 150°C. The electrode kinetics have been compared with methane and other small hydrocarbons in acid media. The formation of strongly adsorbed CO has been observed in all cases. Fourier Transform Infrared Reflectance (FTIR) studies in a thin-layer external

reflectance cell indicate that the linearly adsorbedCO(ads) is the predominant form on single crystal Pt surfaces for hydrocarbons (methane, ethane, ethylene) as well as alcohols (methanol, ethanol). Bridge bonded CO(ads) is also observed in some instances with FTIR.

The adsorbed CO is very strongly adsorbed on the platinum surface and blocks the catalytic sites needed for the earlier stages of the electrode reaction. This adsorbed CO can be oxidatively desorbed at quite anodic potentials but this is not attractive for fuel cell systems operating on ethane and other small organisms since the cell voltage would be low. This research has demonstrated, however, that this problem is substantially lessened at higher temperatures (>150°C). The use of platinum alloy catalysts (*e.g.*, Pt with Ru, Sn, Mo) results in even faster kinetics. Pronounced structural sensitivity has been observed on the three low index planes. The activity of these surfaces for the oxidation of all the small organic molecules examined ranked in the order Pt(100) > Pt(111) > Pt(110).

2. Electrochemical and infrared properties of CO on platinum

The electrochemical oxidation of CO and reduction of CO_2 have been studied using *in situ* FTIR spectroscopic and electrochemical techniques on single crystal platinum electrodes. The catalytic activity of the low index Pt surfaces for both CO oxidation and CO_2 reduction decreased in following order: (100) > (110) > (111). On Pt(110), the only detectable reduction product of CO_2 was adsorbed CO in linear form on the Pt(110) and (111) surfaces and simultaneously in both the linear and bridge bound forms on Pt(100). The oxidation of the reduction product (*i.e.*, adsorbed CO) indicated similar oxidation peak features in the voltammetry curves to those of the oxidation of CO (from the electrolyte) on those single crystal surfaces. The presence of strongly adsorbed anions such as bisulfate anions or chlorides either gives rise to the steric hindrance,

impeding attack by oxygen donors or inhibits the formation of Pt surface hydroxide, resulting in the retardation of the CO oxidation peaks.

The very sharp CO oxidation voltammetry peaks are interpreted as due to the coupling of two surface processes, *i.e.*, oxidative desorption of CO coupled to anionic adsorption (*e.g.*, Cl^- HSO_4^-, $H_2PO_4^-$, OH^-). Based on the number of electrons transferred during the electrochemical process, reaction mechanisms for oxidation of adsorbed CO and solution phase CO have been proposed.

3. The use of electronic conducting oxides as catalysts and catalyst supports for O_2 reduction

Lithiated nickel oxide [(Li)\NiO] is not active as an electrocatalysts for O_2 reduction in acid aqueous solutions. In alkaline solutions, the oxide exhibits some activity for O_2 reduction but the reaction proceeds by a two-electron reduction to peroxide. At elevated temperatures, however, this oxide becomes surprisingly active, yielding close to 4-electrons per O_2 at 200°C in concentrated KOH with little activation overpotential. With platinum catalysts supported on mosaic (Li)NiO crystals, the electrochemical reduction of O_2 is inhibited at room temperature because of the p-type semiconductor properties of the (Li)NiO. At elevated temperatures (~150°C), however, this oxide in powdered high area form does show promise as a support for Pt. Above 150°C, (Li)NiO itself catalyzes the O_2 reduction in concentrated KOH and the contribution of the supported dispersed Pt is relatively small even in high area form.

In contrast to the behavior of transition metal macrocycle complexes on carbon and graphite surfaces, the cobalt tetrasulfonated phthalocyanine (CoTsPc) does not adsorb strongly on the (Li)NiO oxide or other oxides such as tin-doped indium oxide (ITO). The O_2 reduction in this system proceeds through a peroxide mechanism with the CoTsPc as a solution phase redox

mediator. Well defined solution phase redox couples of CoTsPc were found with ITO electrodes while some of these couples were not observed on the (Li)NiO due to the p-type semi-conductor character of the lithiated nickel oxide.

4. Structural studies of adsorbed transition metal macrocylces complexes on graphite surfaces

Electrochemical studies with *in situ* and *ex situ* STM and AFM have been carried out on highly ordered pyrolytic graphtie surfaces (HOPG). Most of the features of HOPG at atomic level resolution are reasonably well explained theoretically and provide the background needed for understanding the imaging mechanisms. Artifacts encountered with the HOPG surfaces include the multiple tip effects, tip length effects, mairè patterns and thermal drifting. They complicate the interpretation of the STM and AFM results.

The Co- and Fe-tetrasulfonated phthalocyanines (TsPc) adsorbed on an HOPG surface were studied by cyclic voltammetry, AFM, and *in situ* STM. Based on a set of AFM topographies obtained in air for macrocycle molecules preadsorbed on HOPG at monolayer coverage, it is concluded that both the adsorbed Co- and FeTsPc molecules are skew to the surface in parallel planes with the metal cation of one plane coordinated to the nitrogen of the next plane. The tilt angles can be estimated from the molecular size and corrugation heights of the molecular features.

With macrocycle species in an H_2SO_4 electrolyte solution saturated with air, *in situ* STM and AFM images provide evidence that the adsorbed macrocycle molecules are oriented parallel to the HOPG substrate. Different orientations observed with the *ex situ* AFM and also *in situ* STM and AFM measurements are explained on the basis of differences in the various specimen preparation procedures.

"Sheet-type" polymeric transition-metal phthalocyanines were synthesized and characterized by using traditional chemical methods, including FTIR spectroscopy, UV-visible spectroscopy, elemental analysis, ESCA and acid-base titrations. The structures of the p-CoPc and p-FePc obtained from these conventional measurements are in agreement with those obtained from the AFM measurements. The sheet-type polymers were predominantly in rectangular rather than linear arrays. In alkaline solution, both the polymer p-FePc and monomer FeTsPc were found to catalyze the 4-electron reduction of O_2 to OH^- where as the corresponding Co complexes catalyzed the 2-electron O_2 reduction to the peroxide.

This research has demonstrated the power of STM and AFM in the study of electrocatalytic systems, especially the surface structures of electrodes and the orientation of adsorbed species on electrode surfaces. Such measurements are far from routine, however, because of the large number of artifacts that enter into the imaging.

C. Continuing Research

While the ONR support of this project terminated on 30 September 1993, some of the research is being continued under a ARPA/ONR/URI project on methanol-air fuel cells in the Case Center for Electrochemical Sciences at Case Western Reserve University with Prof. Robert Savinell as director of the overall project and with Dr. Donald Tryk responsible for the air cathode and related catalyst research. Prof. Yeager is in an advisory capacity as an emeritus faculty member.

Some of the transition metal complexes are of special interest for the methanol air-cell application because they catalyze the 4-electron reduction of O_2 and at the same time are not adversely affected by methanol or its oxidation products which diffuse from the anolyte into the

catholyte through polymer membrane electrolytes such as duPont Nafion 117 and Dow 560. These catalysts, however, are usually not stable for operation over even a few hours in concentrated acids. To achieve stability it has been necessary to partially pyrolyze these macrocycle catalysts on high area carbon supports. This treatment, however, interferes with the efforts to fine tune the redox properties of the porphyrins and its O_2 adducts for the 4-electron oxygen reduction process. The use of solid ionomer electrolytes such as Nafion stabilizes the macrocycles adsorbed on a graphite support and may make it possible to avoid the use of pyrolysis to stabilize these catalysts.

The sheet type polymer macrocycles are expected to be more strongly adsorbed on graphite than the corresponding monomers. The poly-iron phtholocyanine has been found to promote the 4-electron reduction of O_2 in alkaline electrolytes and we anticipate that other sheet type complexes will be found which are good catalysts for the 4-electron reduction.

We have recently found that the transition metal ions can be strongly adsorbed on the surface of some electronic conducting polymers such as heat-treated poly acrylonitrile. These layers are rather similar to the transition metal macrocycles and their behavior as O_2 reduction catalysts is promising.

II. Research Personnel Funded Through This Grant

A. Principal Investigator

1. Ernest B. Yeager, Hovorka Professor of Chemistry, Emeritus

B. Co-Principal Investigator

2. B.D. Cahan, Research Scientist

C. Graduate Students

1. InTae Bae, Ph.D., CWRU, 1989
   Thesis: *In situ* Infrared Spectroscopic Studies of Electrocatalytic Systems

2. Rongrong Chen: Ph.D., CWRU, 1993
   Thesis: Applications of Scanning Probe Microscopy to Electrocatalytic Systems

3. Francis H. Feddrix: Ph.D., CWRU, 1989
   Thesis: The Electrochemical Oxidation of Methanol on Single Crystal Surfaces of Platinum

4. M. Hsiao, Ph.D., CWRU, 1990
   Thesis: Electrochemical Oxidation of Glucose in Single Crystal Surfaces of Gold

5. Haito Huang, Ph.D., CWRU, 1992
   Thesis: The Role of Adsorbed Species in Various Electrocatalytic Processes: Electrochemical and *In Situ* Infrared Spectroscopic Studies

6. S. Andrew Lin: Ph.D., CWRU, 1991
   Thesis: The Electrochemistry of Carbon Monoxide

7. Peter W. Faguy: Ph.D., CWRU, 1989
   Thesis: Applicationsof Fourier Transform Infrared Spectroscopy to Electrochemical Systems

8. Jay Prakash, Ph.D., CWRU,
   Thesis: Oxygen Electrocatalysis on Ruthenium Metal and Its Pyrochlores

9. Zhiwei Zhang: Ph.D., CWRU, 1993
   Thesis: Oxygen Reduction on Lithiated Nickel Oxide as a Catalyst and as a Catalyst Support

10. Qingjuin Zhao: Ph.D., CWRU, 1993
    Thesis: The Electrocatalytic Oxidation of Small Organic Molecules on Platinum

D. Postdoctoral Research Associates

1. Z. Y. Zing: macrocycle catalysts

2. C. Wang: nickel oxides as catalyst and catalyst supports

3. K. Sashikata: O_2 electrocatalysis, FTIR

E. Senior Research Associates

1. Donald Tryk: O_2 electrocatalysis; transition metal oxides

2. S. Gupta: electrochemistry of transition metal complexes

F. Visiting Scientist
Radoslav Adzic, Director, Institute of Electrochemistry, Belgrade, Yugoslavia; now permanently at Brookhaven National Laboratory

III. Publications, Presentations, Patents, Reports Based on ONR Research

A. Publications in Refereed Journals

1. A.A. Tanaka, C. Fierro, D.A. Scherson and E. Yeager, "Oxygen Reduction on Adsorbed Iron Tetrapyridinoporphyrazine," Materials Chemistry and Physics, 22, 431-456 (1989).

2. R.R. Adzic, M.W. Hsiao and E.B. Yeager, "Electrochemical Oxidation of Glucose on Single Crystal Gold Surfaces," J. Electroanal. Chem., 260, 475-485 (1989).

3. I. T. Bae, X. Xing, D. Scherson and E.B. Yeager, "Ionic Transport Effects in *In situ* Fourier Transform Infrared Reflection Absorption Spectroscopy," J. Anal. Chem., 61, 1164-1167 (1989).

4. S. Gupta, D. Tryk, I. Bae, W. Aldred and E. Yeager, "Heat Treated Polyacrylonitrile-Based Catalysts for Oxygen Electroreduction," J. Applied Electrochem. 19, 19-27 (1989).

5. I.T. Bae, X. Xing, C.C. Liu and E.B. Yeager, "*In-situ* Fourier Transform Infrared Reflection Absorption Spectroscopic Studies of Glucose Oxidation on Platinum in Acid," J. Eectroanal. Chem., 284, 335-349 (199).

6. D. Chu, D. Tryk, D. Gervasio and E.B. Yeager, "Examination of the Ionomer/Electrode Interface Using the Ferric/Ferrous Redox Couple," J. Electroanal. Chem., 272, 277-284-(1989).

7. M.S. Hossain, D. Tryk and E. Yeager, "The Electrochemistry of Graphite and Modified Graphite Surfaces: The Reduction of O_2 ," Electrochim. Acta, 34, 1733-1737 (1989).

8. D. Chu, D. Gervasio, M. Razaq and E.B Yeager, "Infrared Reflectance Absorption Spectroscopy (IRRAS). Study of the Thermal Stability of Perfluorinated Sulphonic Acid Ionomers on Pt," J. Appl. Electrochemistry, 20, 157-162 (1990).

9. I.T. Bae, D. Scherson and E.B. Yeager, "Infrared Spectroscopic Determination of pH Changes in Diffusionally Decoupled Thin-Layer Electrochemical Cells," J. Anal. Chem., 62, 45-49 (1990).

10. J. Prakash, D. Tryk and E.B. Yeager, "Electrocatalysts for Oxygen Electrodes in Fuel Cells and Water Electrolyzers for Space Applications," J. Power Sources, 29, 413-422 (1990).

11. P.W. Faguy, N. Markovic, R.R. Adzic, C.A. Fierro and E.B. Yeager, "A Study of Bisulfate Adsorption on Pt(111) Single Crystal Electrodes Using *in situ* Fourier Transform Infrared Spectroscopy," J. Electroanal. Chem., 289, 245-262 (1990).

12. B.Z. Nikolic, H. Huang, D. Gervasio, A. Lin, C. Fierro, R.R. Adzic and E.B. Yeager, "Electroreduction of Carbon Dioxide on Platinum Single Crystal Electrodes: Electrochemical and *in situ* FTIR Studies," J. Electroanal. Chem., 295, 415-423 (1990).

13. D. Ohms, S. Gupta, D.A. Tryk, E. Yeager and K. Wiesener, "ESCA and Electrochemical Studies of chelate-Modified Carbon Materials for Cathodic Oxygen Reduction," Z. physik. Chem., 272, 451-459 (1990).

14. D. Aurbach, M. Daroux, P. Faguy and E. Yeager, "The Electrochemistry of Noble Metal Electrodes in Aprotic Organic Solvents Containing Lithium Salts," J. Electroanal. Chem., 297, 225-244 (1991).

15. H. Huang, C. Fierro, D. Scherson and E.B. Yeager, "*In Situ* Fourier Transform Infrared Spectroscopic Study of CO_2 Reduction on Polycrystalline Platinum in Acid Solutions," Langmuir, 7, 1154-1157 (1991).

16. S. Gupta, C. Fierro and E. Yeager, "The Effects of Cyanide on the Electrochemical Properties of Transition Metal Macrocycles for Oxygen Reduction in Alkaline Solutions, J. Electroanal. Chem., 306, 239-250 (1991).

17. B. Cahan, M. Villullas and E. Yeager, "The Effects of Trace Anions on the Voltammetry of Single Crystal Gold Surfaces," J. Electroanal. Chem., 306, 213-238 (1991).

18. I.T. Bae, E. Yeager, X. Xing and C.C. Liu, "*In* situ Infrared Studies of Glucose Oxidation on Platinum in an Alkaline Medium," J. Electroanal. Chem., 309, 131-145 (1991).

19. I.T. Bae, H. Huang, E.b. Yeager, and D.A. Scherson, "*In Situ* Infrared Spectroscopic Studies of Redox Active Self-Assembled Monolayers on Gold Electrode Surfaces, Langmuir, 7, 1558-1562 (1991).

20. Z.Y. Zeng, S.L. Gupta, H. Huang and E.B. Yeager, "Oxygen Reduction on Poly(4-vinylpyridine)-Modified Ordinary Pyrolytic Graphite Electrodes with Adsorbed Cobalt Tetra-sulphonated Phthalocyanine in Acid Solutions," J. Appl. Electrochem., 21, 973-981 (1991).

21. S. Gupta, H. Huang and E. Yeager, "Studies of Adsorption of Tetrasulfonated Phthalocyanines on Graphite Substrate," Electrochim. Acta, 36, 2165-2169 (1991).

22. M.W. Hsiao, R.R. Adzic and E.B. Yeager, "The Effects of Adsorbed Anions on the Oxidation of D-Glocose on Gold Single Crystal Electrodes," Electrochim Acta, 37, 357-363 (1992).

23. R.R. Adzic, M.W. Hsiao, E.B. Yeager and G. Pruett, "Scanning Tunneling Microscopy of Stepped Single Crystal Surfaces of Gold," Surface Sci. Lett., 273, L425-L429 (1992).

24. F.H. Feddrix, E.B. Yeager and B.D. Cahan, "Low Energy Electron Diffraction and Cyclic Voltammetry Studies of Flame-Annealed Platinum Single Crystals," J. Electroanal. Chem., 330, 419-431 (1992).

25. R. Adzic, F. Feddrix, B.Z, Nikolic and E. Yeager, "The Elucidation of Hydrogen and Anion Adsorption on Pt(111) through the Co-Adsorption of Metal Adatoms and Carbon Monoxide," J. Electroanal. Chem., 34, 287-306 (1992).

26. Aurbach, M. Daroux, G. McDougal and E.B. Yeager, "Spectroscopic Studies of Lithium in an Ultrahigh Vacuum System," J. Electroanal. Chem., 358, 63-67 (1993).

B. Publications in Non-Refereed Proceedings, Monographs, Etc.

1. R.R. Adzic, D. Gervasio, I. Bae, B. Cahan, and E. Yeager, "Tritium Measurements and Deuterium Loading in D_2O Electrolysis with a Palladium Cathode," Proceedings of the First Annual Conference on Cold Fusion, March 28-31, 1990, National Cold Fusion Institute, Salt Lake City, Utah, pp. 261-271.

2. E. Yeager, M. Razaq, D. Gervasio, A. Razaq and D. Tryk, Proceedings of the Workshop on Structural Effects in Electrocatalysis and Oxygen Electrochemistry, Cleveland, OH, Oct. 29-Nov. 1, 1991, The Electrochemical Society, Vol. 92-11, pp. 440-473.

3. J. Prakash, D. Tryk, W. Aldred and E. Yeager, "Transition-Metal Oxide Electrocatalysts for O_2 Electrodes: The Pyrochlores," in Electrochemistry in Transition, O.J. Murphy, S. Srinivasan and B.E. Conway, eds., Plenum Press, New York, 1992, pp. 93-106.

4. Daniel A. Scherson and Ernest B. Yeager, "Applications of Spectroscopic Techniques to the *In situ* Study of Electrochemical Interfaces," Chapter 7, *Physical Methods of Chemistry*, 2nd ed., Vol. IXB, Bryant W. Rossiter and Roger C. Baetzold, editors, J. Wiley and Sons, New York, 1993.

C. Patents: None

D. Invited Presentations at Conferences, National and International Meetings

1. E. Yeager, J. Prakash, D. Tryk and W. Aldred, "Transition Metal Oxide Electrocatalysts for O_2 Electrodes: The Pyrochlores," The Third Chemical Congress of North America, June 5-10, 1988, Toronto, Canada.

2. E. Yeager, "*In-situ* Optical Studies of Electrocatalysis,"The 40th Meeting of the International Society of Electrochemistry, Kyoto, Japan, September 17-22, 1989.

3. E. Yeager, B.z. Nikolic, H. Huang, D. Gervasio, A. Lin, C. Fierro and R.R. Adzic, "Effect of the Crystallographic Orientation of Pt on CO_2 Electroreduction: Electrochemical and *in situ* IR Studies," The Electrochemical Society National Meeting, Washington, DC, May 5-10, 1991, Extended Abst. 91-1, 690.

4. E. Yeager, "Opportunities for O_2 Cathodes in Batteries, Fuel Cells and Industrial Electrolytic Processes," Vittorio de Nora Award Address at the 181st National Meeting of the Electrochemical Society, Inc., St. Louis, Missouri, May 17-22, 1992.

5. E. Yeager, M. Razaq, D. Gervasio, A. Razaq and D. Tryk, "The Electrolyte Factor in O_2 Reduction Electrocatalysis," Proceedings of the Workshop on Structural Effects in Electrocatalysis and Oxygen Electrochemistry, Case Western Reserve University, Oct. 29-Nov. 1, 1991. The Electrochemical Society, Inc., Pennington, NJ, pp. 440-473.

E. Contributed Presentations and Papers at Scientific Meetings and Workshops

1. R.R. Adzic, F. Feddrix and E. Yeager, "The Elucidation of Hydrogen and Anion Adsorption on Pt(111) Through the Co-Adsorption of Metal Adatoms and CO," The Electrochemical Society, National Meeting, Hollywood, Florida, Oct. 15-20, 1988, Extended Abst., 89-2, 662.

2. S. Gupta and E. Yeager, "The Effects of Cyanide on the Redox Behavior and Electrocatalytic Properties of Transition Metal Macrocycles for Oxygen Reduction in Alkaline Solutions," loc. cit. Extended Abst., 98-2, 665.

3. I.T. Bae, D.A. Scherson and E.B. Yeager, "Infrared Spectroscopic Determination of pH Changes in Diffusionally Decoupled Thin Layer Electrochemical Cells," loc. cit., Extended Abst., 89-2, 676.

4. H.W. Hsiao, R.R. Adzic, D. Gervasio and E.B. Yeager, "Studies of Glucose Electrooxidation on Gold Surfaces in Phosphate Buffer Using Ex-Situ NMR Spectroscopy," The Electrochemical Society, National Meeting, Montreal, May 6-11, 1990, Extended Abst., 90-1, 661.

5. K. Kanamura, A. Tanaka, D. Gervasio R. Adzic and E.B. Yeager, "Hydrogen Electrosorption on Single Crystal Platinum Surfaces in Aqueous Phosphoric Acid Solutions," loc. cit., Extended Abst., 90-1, 664.

6. A. Tanaka, K. Kanamura, R. Adzic, B. Cahan and E. Yeager, "Oxygen Reduction on Single Crystal Platinum Electrodes," loc. cit., Extended Abst., 90-1, 667.

7. A. Lin, K. Kanamura, R. Adzic and E. B. Yeager, "Electrooxidation of Carbon Monoxide on Single Crystal Platinum Surface in Aqueous," loc. cit., Extended Abst., 90-1, 668.

8. I.T. Bae, F. Feddrix, and E.B. Yeager, "Methanol Oxidation on Platinum Single Crystals of (111), (110), and (100) Faces: *In situ* Infrared Spectroscopic Study," loc. cit., Extended Abst., 90-1, 799.

9. X. Xing and C.C. Liu, "*In Situ* Infrared Studies of Glucose Oxidation on Platinum in an Alkaline Medium," loc. cit. Extended Abst., 90-1, 800.

10. S. Gupta, H. Huang and E. Yeager, "Studies of the Adsorption of Tetrasulfonated Phthalocyanines on Graphite," The Electrochemical Society National Meeting, Seattle, WA, Oct. 14-19, 1990, Extended Abst., 90-2, 64.

11. Z.Y. Zeng, S.L. Gupta, H. Huang and E.B. Yeager, "Oxygen Reduction on Poly(4-Vinylpyridine)-Modified Ordinary Pyrolytic Graphite Electrodes with Adsorbed Cobalt Tetrasulfonated Phthalocyanine in Acid Solutions," loc. cit., Extended Abst. 90-2, 65.

12. M.W. Hsiao, R.R. Adzic and E.B. Yeaer, "The Effects of Anions on the Electrochemical Oxidation of D-Glucose on Gold Single Crystal Electrodes," loc. cit., Extended Abst., 90-2, 714.

13. H. Huang, C. Fierro, D. Scherson and E.B. Yeager, "*In Situ* FTIR Study of CO_2 Reduction on Polycrystalline Platinum Eectrode in 0.1 M HCl_4," loc. cit., Extended Abst., 90-2, 715.

14. B.Z. Nikolic, H. Huang, D. Gervasio, A. Lin, C. Fierro, R.R. Adzic and E. Yeager, "Effect of the Crystallographic Orientation of Pt on CO_2 Electroreduction: Electrochemical and *in* situ IR Studies," The Electrochemical Society National Meeting, Washington, DC, May 5-10, 1991, Extended Abst., 91-1, 690.

15. H. Huang, I.T. Bae, D.A. Scherson, and E.B. Yeager, "Anion Effects on the Redox and Vibrational Properties of Self-Assembled Layers of N, N'-Dialkyl-4,4' Bipyridinium on Pt and Au in Aqueous Solutions," loc. cit., Extended Abst., 91-1, 659.

16. A. Lin, B. Cahan and E. Yeager, "The Oxidation of CO on Polycrystalline Pt Surfaces Using a Hanging Meniscus Rotating Disk Electrode," The Electrochemical Society 180th National Meeting, Phoenix, Arizona, October 13-17, 1991.

17. Qingjun Zhao and Ernest B. Yeager, "*In Situ* Infrared and Electrochemical Studies of the Oxidation of Ethylene on Single Crystal and Polycrystalline Platinum Electrodes," The Electrochemical Society 181st National Meeting, St. Louis, Missouri, May 17-22, 1992, Extended Abst., 92-1, 32.

18. Q. Zhao, F. Feddrix, R. Adzic, D. Tryk and E. Yeager, "The Electrochemical Oxidation of Methanol and Other Small Organic Molecules in Acid Electrolytes," Research Day, Case Center for Electrochemical Sciences, Case Western Reserve University, Cleveland, Ohio, May 16, 1993.

19. Q. Zhao and E.B. Yeager, "*In situ* FTIR Electrochemical Studies of the Adsorption and Oxidation of Ethane on Platinum at Elevated Temperatures, "The Electrochemical Society 183rd National Meeting, Honolulu, Hawaii, May 16-21, 1993.

F. Technical Reports

1. Technical Report 67, P.W. Faguy, N. Markovic, R.R. Adzic, C. Fierro and E. Yeager, "A Study of Bisulfate Adsorption on Pt(111) Single Crystal Electrodes Using in-situ Fourier Transform Infrared Spectroscopy," J. Electroanal. Chem.

2. Technical Report 68, B.D. Cahan, H.M. Villullas and E. Yeager, "The Effects of Trace Anions on the Voltammetry of Single Crystal Gold Surfaces," J. Electroanal. Chem.

3. Technical Report 69, D. Aurbach, M. Daroux, P. Faguy and E. Yeager, "The Electrochemistry of Noble Metal Electrodes in Aprotic Organic Solvents Containing Lithium Salts," J. Electroanal. Chem.

4. Technical Report 70, S. Gupta and E. Yeager, "The Effects of Cyanide on the Electrochemical Properties of Transition Metal Macrocycles for Oxygen Reduction in Alkaline Solutions," J. Electroanal. Chem.

5. Technical Report 71, I.T. Bae, H. Huang, E.B. Yeager and D.A. Scherson, "In-Situ Spectroscopic Studies of Redox Active Self-Assembled Monolayers on Metal Electrode Surfaces," Langmuir.

6. Technical Report 72, I. Bae, H. Huang, E. Yeager and D.A. Scherson, "In-Situ Spectroscopic Studies of Redox Active Self-Assembled Monolayers on Gold electrode Surfaces," Langmuir.

7. Technical Report 73, H. Huang, C. Fierro, D. Scherson and E. Yeager "In-situ FTIR Study of CO_2 Reduction on Polycrystalline Platinum in Acid Solutions," Langmuir.

8. Technical Report 74, R.R. Adzic, M.W. Hsiao and E. Yeager, "Electrochemical Oxidation of Glucose on Single Crystal Gold Surfaces," J. Electroanal. Chem.

9. Technical Report 75, I.T. Bae, X. Xing, D. Scherson and E. Yeager, "Ionic Transport Effects in in-situ Fourier Transform Infrared Reflection Absorption Spectroscopy," J. Anal. Chem.

10. Technical Report 76, S. Gupta, D. Tryk, I. Bae, W. Aldred and E. Yeager, "Heat-Treated Polyacrylonitrile-Based Catalysts for Oxygen Electroreduction," J. Appl. Electrochem.

11. Technical Report 77, I. Bae, X. Xing, C.C. Liu and E. Yeager, "In-situ Fourier Transform Infrared Reflection Absorption Spectroscopic Studies of Glucose Oxidation on Platinum in Acid," J. Appl. Electroanal.

12. Technical Report 78, D. Chu, D. Gervasio, D. Tryk and E. Yeager, "Examination of the Ionomer/Electrode Interface Using the Ferric/Ferrous Redox Couple," J. Electroanal. Chem.

13. Technical Report 79, M.S. Hossain, D. Tryk. and E. Yeager, "The Electrochemistry of Graphite and Modified Graphite Surfaces: The Reduction of O_2," Electrochim. Acta.

14. Technical Report 80, D. Chu, D. Gervasio, M. Razaq and E. Yeager, "Infrared Reflectance Absorption Spectroscopy (IRRAS). Study of the Thermal Stability of Perfluorinated Sulphonic Acid Ionomers on Pt," J. Appl. Electrochem.

15. Technical Report 81, I.T. Bae, D.A. Scherson and E. Yeager, "Infrared Spectroscopic Determination of pH Changes in Diffusionally Decoupled Thin-Layer Eectrochemical Cells," J. Anal. Chem.

16. Technical Report 82, R.R. Adzic, D. Gervasio, B. Cahan, I. Bae and E. Yeager, "Investigation of Phenomena Related to D_2O Electrolysis at a Palladium Cathode," Proceedings of the NSF/EPRI Workshop on Anomalous Effects in Deuterated Materials,

17. *Technical Report 83*, R.R. Adzic, D. Gervasio, I. Bae, B. Cahan and E. Yeager, "Tritium Measurements and Deuterium Loading in D_2O Electrolysis with a Palladium Cathode," Proceedings of the First Annual Conference on Cold Fusion.

18. Technical Report 84, P.W. Faguy, N. Markovic, R.R. Adzic, C.A. Fierro and E.B. Yeager, "A Study of Bisulfate Adsorption on Pt(111) Single Crystal Electrodes Using *in-situ* Fourier Transform Infrared Spectroscopy," J. Electroanal Chem.

19. Technical Report 85, B.z. Nikolic, H. Huang, D. Gervasio, a. Lin, C. Fierro, R.R. Adzic and E. B. Yeager, "Electroreduction of Carbon Dioxide on Platinum Single Crystal Electrodes: Electrochemical and *in-situ* FTIR Studies, "J. Electroanal. Chem.

20. Technical Report 86, S. Gupta, C. Fierro and E. Yeager, "The Effects of Cyanide on the Electrochemical Properties of Transition Metal Macrocycles for Oxygen Reduction in Alkaline Solutions," J. Electroanal. Chem.

21. Technical Report 87, Z.Y. Zeng, S.L. Gupta, H. Huang and E.B. Yeager, "Oxygen Reduction on Poly(4-Vinylpyridine)-Modified Ordinary Pyrolytic Graphite Electrodes with Adsorbed Cobalt Tetra-Sulphonated Phthalocyanine in Acid Solutions," J. Electroanal. Chem.

22. Technical Report 88, S. Gupta, H. Huang and E. Yeager, "Studies of the Adsorption of the Tetrasulfonated Phthalocyanines on Graphite Substrate," Electrochim. Acta.

23. Technical Report 89, M.W. Hsiao, R.R. Adzic and E.B. Yeager, "The Effects of Adsorbed Anions on the Oxidation of D-glucose on Gold Single Crystal Electrodes," J. Electrochimica Acta.

24. Technical Report 90, I.T. Bae, E. Yeager, X. Xing and C.C. Liu, "*In*-situ Infrared Studies of Glucose Oxidation on Platinum in an Alkaline Medium," J. Electroanal. Chem.

25. Technical Report 91, R.R. Adzic, M.W. Hsiao, E.B. Yeager and G. Pruett, "Scanning Tunneling Microscopy of Stepped Single Crystal Surfaces," Surface Sci. Lett.

26. Technical Report 92, F.H. Feddrix, E.B. Yeager and B.D. Cahan, "Low Energy Electron Diffraction and Cyclic Voltammetry Studies of Flame-Annealed Platinum Single Crystals," J. Electroanal. Chem.

27. Technical Report 93, E.B. Yeager, M. Razaq, D. Gervasio, A. Razaq and D. Tryk, "Dioxygen Reduction in Various Acid Electrolytes," J. Serb. Chem. Soc.

28. Technical Report 94, E. Yeager, M. Razaq, D. Gervasio, A. Razaq and D. Tryk, "The Electrolyte Factor in O_2 Reduction Electrocatalysis," Proceedings of the Workshop on Structural Effects in Electrocatalysis and Oxygen Electrochemistry, Cleveland, Oct. 29 - Nov. 1, 1991. The Electrochemical Society, Vol. 92-11, pp. 440-473.

29. Technical Report 95, J. Prakash, D. Tryk, W. Aldred and E. Yeager, "Transition-Metal Oxide Electrocatalysts for O_2 Electrodes: The Pyrochlores," Electrochemistry in Transition, O.J. Murphy, S. Srinivasan and B.E. Conway, eds., Plenum Press, New York, 1992, pp. 93-106.

IV. Transitions: Interactions or Association with Industrial and Government Efforts

1. DOE, subcontract through the Electrosynthesis Corporation (SBIO)

Grant/Project Title:	Modified Carbon Supports for Electrocatalysts
Amount of Funding:	$180,000
Total Period:	9/14/90 - 9/13/92
Research:	The Electrosynthesis Corp. partially fluorinated high area carbon supports for O_2 electro-catalysts with the principal objective of stabilizing the carbon support against oxidation and thus extending the operating life for metal-air batteries and various fuel cells. The Electrosynthesis Corp. partially fluorinated the carbons and the CWRU group then fabricated them into gas-fed O_2 cathodes using its experience gained on the ONR sponsored research with gas-fed high current density air

cathodes. The performance. however, was only marginally better.

2. Eveready Battery Company

Grant/Project Title: Water Management in Zinc-Air Cells
Amount of Funding: $100,000
Total Period: 9/30/92-9/29/93 (Further funding is pending)
Research: A study of factors controlling water gain and loss in small consumer type zinc air cells was carried out at CWRU in collaboration with the Eveready Westlake Laboratory. It appears possible to stabilize such cells against water gain or loss in high and low humidity environments using anion conducting solid polymers as the electrolytes. This cooperative project utilizes experience gained in ONR supported work on O_2 electrodes and polymer electrolytes. If as successful as we expect, this project should result in much more extensive use of zinc air cells. Present miniature cells are limited to a few weeks of use after the seals are removed because of water or loss.

3. ARPA-ONR Project

Grant/Project Title: Methanol-Air Fuel Cells
Amount of Funding: ~$600,000
Total Period: 7/1/92-6/3-/95
Research: Research is in progress on air cathodes for use with new polymer electrolytes operating at temperatures of up to 200°C. Our group is concerned with more active catalysts which are not poisoned or otherwise adversely effected by methanol and its oxidation by products which diffuse from the anolyte into the catholyte through the membrane electrolytes. Various transition metal complexes including the macrocycles are very promising provided their structure can be adequately stabilized as adsorbed layers using solid ionomers as electrolytes with species added to suppress the metal cation solubility.

4. Case Sensor Center/National Institute of Health

Grant/Project Title:	Electrochemical Sensors for L-dopa
Amount of Funding:	$10,700
Total Period:	9/30/91-9/29/92
Research:	Preliminary work was initiated to establish the feasibility of continuously monitoring the level of the L-dopa and other neurotransmitters in the blood and tissue using electrochemical methods. The levels in the brain, however, do not correlate well with the blood levels because of large variations in the permeability of the blood-brain barrier to L-dopa and the major effect of blood proteins on the permeability to L-dopa. Introduction of electrodes in the brain is already being carried out with animals but is not practical with humans. This project has been discontinued for the time being.

V. Three Significant Publications

1. "Low Energy Electron Diffraction and Cyclic Voltammetry Studies of Flame Annealed Platinum Single Crystals," F.H. Feddrix, E.B. Yeager and B.D. Cahan, J. Electroanal.Chem., 330, (1992) 419-431.

The objective of the research described in this publication ws to establish the validity of the Clavilier flame annealing method for preparing platinum single crystal electrode surfaces. A large number of electrochemists have used the Clavilier method in place of the much more tedious and demanding ultra high vacuum-electrolytic solution transfer. With the exception of the work of Fauri, quoted but not published by Aberdam *et al.*, the validity of the Clavilier method has not been examined with low energy electron diffraction.

In this paper, LEED and cyclic linear sweep voltammetry were used to examine the surface structure of flame anealed Pt (100, (110) and (111) electrodes. Well defined LEED

patterns were obtained for these surfaces but only after additional heat treatment *in vacuo* at 400°C in order to remove surface contaminates. The cyclic voltammograms corrresponded to those expected for the low index Pt surfaces from prior studies in our laboratory.

2. "A Study of Bisulfate Adsorption on Pt(111) Single Crystal Electrodes Using *In situ* Fourier Transform Infrared Spectroscopy," P.W. Faguy, N. Markovic, R.R. Adzic , C.A. Fierro and E.B. Yeager, J. Electroanal. Chem., 289, (1990), 245-262.

Subtractively normalized interfacial Fourier transform spectroscopy (SNIFTIRS) has yielded the first spectroscopic evidence that HSO_4^- anion adsorption is associated with the anomalous peaks seen in the cyclic voltammetry of Pt(111) in sulfuric acid. The infrared data indicate that the beginning of bisulfate anion adsorption coincides with the onset of the anomalous peak region on Pt(111). There is no evidence of $SO_4^=$ adsorption over the same potential region. The adsorbed HSO_4^- absorption peak frequency is strongly potential dependent. This increase in peak infrared frequency with increasing potential can be rationalized using molecular orbital arguments. While the high boiling point, stabilization and good conductivity of concentrated sulfuric acid are attractive from the standpoint of fuel cell applications, the strong adsorption of the bisulfate anion inhibits the oxidation of organic species such as methanol in this acid and has provided the motivation to look for new electrolytes including polymer electrolytes.

3. "The Elucidation of Hydrogen and Anion Adsorption on Pt(111) through the Co-Adsorption of Metal Adatoms and Carbon Monoxide," R.R. Adzic, F. Feddrix, B.Z. Nikolic and E. Yeager, J. Electroanal. Chem., 341, (1992) 287-306

Copper, lead and carbon monoxide adsorbates have been used to probe the adsorption processes on a Pt(111) electrode in H_2SO_4 and $HClO_4$ solutions. All three adsorbates cause inhibition of hydrogen adsorption in both solutions and a decrease of the anomalous peak recently ascribed to

HSO_4^- adsorption. The "butterfly" peak in $HClO_4$ solution is slightly perturbed by Cu and Pb adatoms. Evidence was found that the species responsible for the anomalous peak for Pt(111) in H_2SO_4 solutions is not H_{ads} and that HSO_4^- probably interacts with three Pt(111) sites. A twofold interaction of HSO_4^- with the Pt(111) surface, however, cannot be ruled out completely. In $HClO_4$ solutions the Cu and Pb adatoms do not cause any decrease of the charge associated with the "butterfly" peak. These results can be explained in terms of PtOH as the species involved with the "butterfly" peak. The electrosorption valence of HSO_{ads} is unity, which indicates a strong interaction with the surface and a high charge transfer. The Temkin interaction parameter for H_{ads} is $fRT = 42$ kJ mol^{-1}, which provides evidence for a large repulsive interaction of H_{ads} on the Pt(111) surface. It decreases in the presence of Cu and CO adsorbates. These results illustrate the usefulness of the competitive adsorption of various adsorbates in probing adsorption processes on electrode surfaces.

VI. Awards and Honors

1. The Vittorio de Nora Award, The Electrochemical Society, May 1992
   - Awarded biannually for contributions to electrochemical engineering and technology
   - Award includes a gold medal and $5,000
   - Award address: The Electrochemistry of Molecular Oxygen: Mechanistic and Catalylis Aspects

In the award address, Professor Yeager focused on the challenging problem of finding stable catalysts for the overall 4-electron reduction of O_2 in aqueous solutions at low and moderate temperatues. Many catalysts are available for the 2-electron reduction to the peroxide

state. Such peroxide forming catalysts can be used in conjunction with a peroxide decomposition catalyst to achieve the overall 4-electron reduction. This pathway, however, leads to excessive polarization. Consequently catalysts promoting the direct 4-electron reduction are preferred to achieve high operating potentials. The lecture reviews the factors that must be considered in developing 4-electron reduction catalysts. Several 4-electron reduction catalyst are considered from the standpoint of reaction mechanisms and factors controlling the operating potential of the O_2 cathode; these include platinum, transition metal macrocycle complexes and the pyrochlors. The lecture also considered how electrolyte factors influence catalytic activity (including the use of solid ionomers and self-assembling layers on the electrode surface).

2. The renaming of the Case Center for Electrochemical Sciences as the

   Ernest B. Yeager Center for Electrochemical Sciences in honor of its founder.

   - The renaming will be combined with a one-day symposium on electrochemistry to be held on September 22, 1994 with Prof. R. Marcus, Prof. Gabor Somorjai and W. John Albery.

FINAL REPORT DISTRIBUTION LIST - GENERAL

Dr. Robert Nowak (1)*
Office of Naval Research
Chemistry and Physics Division, ONR 311
Ballston Tower 1, Room 503
800 North Quincy Street
Arlington, Virginia 22217-5660

Defense Technical Information
Center (2)*
Building 5, Cameron Station
Alexandria, VA 22314

* Number of copies to forward